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Pyrolysis using microwave absorbents as reaction bed: an improved approach to transform used frying oil into biofuel product with desirable properties

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Abstract

Used frying oil (UFO), a waste produced in large volume each year worldwide, represents a potential resource for biofuel production rather than a disposal problem for modern society. Pyrolysis technique using microwave heating offers a promising approach for the conversion of UFO into biofuel products with improved properties. In this study, pyrolysis of UFO was performed by contacting with a bed of microwave absorbents heated by microwave radiation. The pyrolysis approach was examined using different materials as the reaction bed, comprising particulate carbon, activated carbon and mesoporous aluminosilicate (MCM-41). The use of particulate and activated carbon as the reaction bed provided a fast heating rate and extensive cracking capacity to pyrolyze the used oil, thus showing favorable features that could lead to short process time and less energy usage. This resulted in a production of a high yield of a biofuel product (up to 73 wt%) in a process taking less than 35 min. The biofuel showed a composition dominated by light C₅-C₂₀ aliphatic hydrocarbons with low amounts of oxygenated compounds ($\leq 11\%$). In particular, the oil product obtained from activated carbon bed showed a low nitrogen content and was free of carboxylic acid and sulphur. The absence of carboxylic acids with low amounts of oxygenated compounds could reduce the formation of oxygenated by-

products that could generate undesirable acidic tar or potentially hazardous sludge in the biofuel during storage. Combined with the detection of a high calorific value (46 MJ/kg) nearly comparable to diesel fuel, the biofuel shows great promise to be upgraded for use as a ‘cleaner’ fuel source with potentially reduced oxygenated by-products plus low or zero emissions of NO_x and SO_x during the use of the fuel in combustion process. This study also revealed that the use of activated carbon bed results in the highest energy recovery (88-90%) from the used frying oil. Our results demonstrated that the use of a microwave-heated reaction bed of activated carbon shows great potential as an improved and sustainable pyrolysis approach that is energy-efficient and timesaving for the recycling of used frying oil into a biofuel product with desirable properties. This pyrolysis approach provides an alternative to transesterification that avoids the use of solvents and catalysts, and thus could be developed further as a promising route to recycle various types of waste and biomass materials.

Keywords: Pyrolysis; Microwave; Absorbent; Oil; Biofuel; Cooking oil

1. Introduction

Used frying oils (UFO) are produced by frying at temperatures ranging from 160 °C to 200 °C in municipal households and restaurants. Due to its ease of acquisition and low cost, the vegetable oil is widely used in the catering business and this causes problems when the oil is inefficiently managed and disposed. There are approximately 29 million tons of UFO being produced each year throughout the world (Maddikeri et al., 2012).

Pyrolysis has been researched as a technique to produce biofuel from triglycerides-based materials such as soybean oil, castor oil, and palm oil (Lima et al., 2004; Phung et al., 2015). It is a thermochemical conversion process that heats materials at high temperature (300 – 1000 °C) in the absence of oxygen to produce char residue, bio-oil and gases as the pyrolysis product. Several researchers have investigated the feasibility of pyrolysis using conventional heating sources (e.g. furnace, electric oven) to transform biomass material into high energy products (Dunnigan et al., 2016; Lim et al., 2016; Mohammed et al., 2016; Zhong et al., 2010; Zubrik et al., 2017). It was found that these pyrolysis processes often require a long process time (≥60

min) while producing undesirable yield of bio-oil (≤ 40 wt%), probably due to the inefficient heat transfer shown by the use of furnace or electric oven as a heating source. These result in increased energy usage, heat losses, and production cost since more time and energy are required to heat the material to the target temperature in order for pyrolysis conversion to occur. Also, the long process time can promote undesired secondary cracking that could lead to the high oxygen content (≥ 30 wt.%) of the bio-oil product. Owing to the limitation shown by conventional pyrolysis techniques, microwave pyrolysis has been proposed as an alternative to enhance the heating and cracking mechanism in pyrolysis process (Lam et al., 2016a; Lucas-Torres et al., 2016; Mubarak et al., 2014). This type of pyrolysis process involves the use of microwave as the heating source and is reported to offer advantages such as fast heating, uniform heat distribution, and better control over the heating process compared to the use of conventional heating (e.g. furnace)(Lam et al., 2016c).

There has even been a different approach proposed recently for microwave pyrolysis in which the target material is pyrolyzed by contact with a bed of microwave absorbent heated by microwave radiation. The bed of microwave-absorbent absorbs enough microwave energy and heats up to achieve the desired temperature for pyrolytic thermal cracking, and subsequently act as a reaction bed to crack waste and biomass materials to produce a variety of different products (Lam et al., 2015; Lam et al., 2016b; Lam et al., 2012b; Lam et al., 2016d; Russell et al., 2012; Wan Mahari et al., 2016).

The use of microwave absorbent as a reaction bed shows good heat transfer as microwave energy can efficiently penetrate the absorbent being heated and in turn generates heat throughout the volume of the absorbent. The absorbent can then transfer the heat to the targeted materials via short-range conduction for pyrolysis cracking. Short heat transfer distances, the enveloping

nature of the well-mixed reaction bed, and small particle size of the microwave absorbent used (with corresponding large surface area) make this an efficient method that allows rapid heating to high temperature in order for extensive pyrolysis cracking to occur, and thus providing an energy-efficient heating process and facilitating increased production rates or savings in process time. Moreover, the microwave energy is targeted only to the reaction bed of microwave absorbent and not to gases within the heating chamber or the chamber itself. It can promote certain chemical reactions by selectively heating the reactants, leading to a more uniform temperature profile and improved yield of desirable products. In addition, the rapid heating promoted by the reaction bed could activate dehydration reaction mechanism to evaporate and remove the water inherent in the waste and biomass materials, which could lead to reduction of water (an undesirable substance) in the resulting bio-oil product.

A variety of materials such as metal oxide, charcoal-derived carbon, activated carbon, silicon carbide and silica-alumina based materials have been used as microwave absorbents in microwave pyrolysis process (Borges et al., 2014; Lam et al., 2012a; Russell et al., 2012; Suriapparao and Vinu, 2015). Although metal oxide has been reported to effectively absorb microwave radiation and enhance the heating rate (Mushtaq et al., 2014), the metallic material could reflect the microwave radiation back towards the magnetron and in turn cause damage to the magnetron while also create difficulty in monitoring and controlling the pyrolysis temperature (Peng and Hwang, 2015). Previous study also reported that the use of metal powders under microwave conditions resulted in very destructive electrical arcing that was uncontrollable (Whittaker and Mingos, 2000).

Carbonaceous materials have high microwave absorbency and heat tolerance, thus they have also been investigated as a microwave absorbent in microwave pyrolysis process (Abubakar

et al., 2013; Lam et al., 2012b). A high yield (88 wt.%) of oil product with fuel properties comparable to transportation fuels was obtained by Lam et al. (2012a) from the use of particulate carbon to pyrolyze waste automotive engine oil (Lam et al., 2012a). The oil product was also free with low levels of sulphur, oxygen and toxic PAH compounds. Russell et al. (2012) found that the use of activated carbon produced greater pyrolysis cracking of high density polyethylene (HDPE) that generated a light oil product with a carbon chain length profile comparable to petroleum-based fuels (Russell et al., 2012).

In view of the promising features shown by the use of a reaction bed of microwave absorbent heated by microwave radiation, this provides the motivation for this study, which is to investigate the use of different microwave absorbents as both the heating medium and reaction bed to pyrolyze UFO. Particulate carbon (PC), activated carbon (AC) and mesoporous aluminosilicate (MCM-41) were selected due to their ease of acquisition. Work has been performed with the objective of investigating the influence of the use of different types of microwave absorbents as the reaction bed on the heating profile, product yield, and composition of the bio-oil. These evaluations are important to assess the feasibility of developing this pyrolysis approach as an improved and sustainable method to convert UFO to produce a liquid biofuel with desirable properties. No similar studies have been reported on the application of this pyrolysis approach in the conversion of used frying oils to produce biofuel product.

2. Materials and methods

2.1 Preparation of UFO and microwave absorbers

UFO originally derived from palm oil was collected from a fried chicken restaurant in Kuala Terengganu, Malaysia. The UFO was collected after the oil was repeatedly reused to fry

fried chickens at temperature ranging from 170 to 200 °C for five days. It was filtered by Whatman No. 4 filter paper to remove suspended food particles. The filtered oil was collected and stored in glass bottles wrapped with aluminium foil. The glass bottles were filled up completely to prevent oxidation of the oil during storage. The compositions and characteristics of UFO were examined and presented in Table 1.

AC made of coconut husk, PC made of charcoal, and mesoporous aluminosilicate type MCM-41 were used as both the microwave absorbent and reaction bed to heat and pyrolyze the UFO. Elemental analysis was performed using CHNS-O Analyzer FLASH EA 1112 Series (Thermo Scientific, USA) to determine the content of carbon, hydrogen, nitrogen, sulphur and oxygen. ASAP 2020 (Micrometrics Ins. Corp.) was used to determine the porous characteristics of the microwave absorbers (i.e. surface area, micropore volume, total pore volume and average pore diameter). This was performed by degassing 0.4 g of microwave absorber at 300 °C with high purity nitrogen gas for 3 h. The degassed absorber was then exposed to nitrogen gas over a range of pressures at a temperature of 77 K, and the volume of N₂ adsorbed and desorbed (cm³/g) on the absorber 's surface at the relative pressure ranging from 0 to 1 were recorded to plot the N₂ adsorption and desorption isotherms. The specific surface area of the absorbers were calculated by the BET (Brunauer, Emmett, and Teller) equation. Micropore volume was calculated based on the t-plot method, whereas the total pore volume was determined at P/P₀ of 0.99 and the average pore diameter was calculated by 4V/S_{BET} equation (Chen et al., 2014); P/P₀ refers to relative pressure derived from equilibrium pressure (P) divided by saturation pressure (P₀), and V refers to the total pore volume and S_{BET} refers to BET surface area of the pores. The resulting specifications of the microwave absorbers are presented in Table 2 (Section 3.1).

2.2 Microwave pyrolysis experiments on UFO

A microwave oven with a frequency of 2.45 GHz was modified to house a quartz pyrolysis reactor (150 x 100 x 100 mm) that was connected to a condensation apparatus. Fig. 1 illustrates the schematic diagram of the microwave pyrolysis apparatus. Approximately 150 g of microwave absorbent (i.e. AC, PC, or MCM-41) was inserted into the pyrolysis reactor to form the reaction bed. 100 g of UFO was then added to the reactor and the mixtures were stirred to ensure an even heat distribution during the pyrolysis process. Then, the microwave oven was switched on to heat the bed of microwave absorbent and UFO from room temperature to the target process temperature ranging from 350 °C to 550 °C. A stainless steel type K thermocouple connected to an electronic temperature controller was used to measure the temperature of the bed of microwave absorbent mixed with the UFO within the reactor. The bed of microwave absorbent is the heating medium that mainly absorb and convert microwave energy to heat and pyrolyze the UFO, and the thermocouple probe is in direct contact with both the bed of microwave absorbent and the UFO in the reactor during experiment, thus the temperature shown by the thermocouple should give a reliable reading of the average temperature of the bulk bed as reported in previous work (Lam et al., 2012b; Lam et al., 2016d). In addition, an infrared thermometer was used to validate the temperature recorded by the thermocouple, and the results showed good precision with low standard deviations shown between the readings from the two devices ($\pm 1-3$ °C). The magnetrons of the microwave oven were also controlled by the electronic temperature controller that maintains the temperature at the set point within a user-specified tolerance by switching the magnetrons on and off appropriately. When the microwave oven had been heated to the target process temperature, the temperature controller functioned to maintain

the oven at the target temperature. Nitrogen gas at a flow rate of 0.2 L/min was purged into the reactor to maintain an inert pyrolysis atmosphere.

The pyrolysis volatiles generated during the pyrolysis of UFO were condensed and collected in the 1st and 2nd collecting vessels as bio-oil, and the remaining volatiles left the reactor as non-condensable pyrolysis gases. The weight increase in the collecting vessels were measured to obtain the yield of bio-oil. It was previously found that a small amount of bio-oil was obtained in the 2nd collecting vessel (<1 wt%), thus the collected bio-oil was mixed with the bio-oil obtained in 1st collecting vessel for further analysis. The gas yield was obtained by calculating the mass difference (i.e. 100 wt% – yield of bio-oil – yield of char residues = gas yield). The char residues were collected after the reactor was cooled to room temperature and the yield was determined by calculating the weight of the reactor and its content before and after pyrolysis.

2.3 Analytical methods

Elemental content (i.e. hydrogen, carbon, sulphur, nitrogen and oxygen) of oil samples was determined using Vario MACRO Elemental Analyzer (Elementar Analyseysteme GmbH). Oxygen was used in the combustion process, whereas helium was used as a carrier gas. The oxygen content was obtained by the mass difference and the results were presented in weight percentage.

The chemical compositions of bio-oil were determined using a 6890 GC-MS instrument (Agilent Technologies). The compounds were separated using a column HP-5MS (length 30 m, film thickness 0.25 µm, diameter 250 µm, stationary phase: 5% Phenyl Methyl Siloxane). The initial temperature of the oven was set at 30 °C with a holding time of 1 min. The oven

temperature was then programmed from 30 °C to 300 °C at a heating rate of 5 °C/min. Helium gas at a constant flow rate of 7 mL/min was used as a carrier gas. The compounds were identified by matching their mass spectra to the NIST 2005 mass spectra database. Each compound is quantified by the integrated area of the corresponding peak on the mass spectrometer chromatogram. The concentration of each compound was calculated as a percentage of the total area of all peaks in the analysis. The calorific value of the oil sample was obtained using a 1341 Plain Jacket bomb calorimeter instrument, according to ASTM D240.

3. Result & discussion

3.1 Characterization of microwave absorbents as reaction bed material

3.1.1 N₂ adsorption-desorption isotherm

Fig. 2(a) shows that AC exhibits a Type I isotherm according to the International Union of Pure and Applied Chemistry (IUPAC), indicating that the AC has a microporous structure. Type I isotherm is an indication of microporous structure where the amount of N₂ adsorption is high and the volumes adsorbed increases sharply at the low relative pressure region ($P/P_0 < 0.2$) and then approaches a limiting value as $P/P_0 \rightarrow 1$ (Chen et al., 2014; Tehrani et al., 2015); P/P_0 refers to relative pressure derived from equilibrium pressure (P) divided by saturation pressure (P_0). The data from the isotherm were calculated for determination of the surface area. The results showed that AC possesses a high adsorption capacity with a BET surface area recording up to 850 m²/g (Table 2), which is within the normal range of surface area reported generally for AC (400-1500 m²/g) (Dinçer et al., 2007).

PC exhibits a Type IV isotherm containing a hysteresis loop (Fig. 2(b)). The hysteresis loop is related to the occurrence of capillary condensation (Gómez-Serrano et al., 2001) that

indicates the presence of a mesoporous structure. However, PC showed a much lower BET surface area ($7.18 \text{ m}^2/\text{g}$) compared to AC but a higher surface area than MCM-41 ($6.13 \text{ m}^2/\text{g}$) (Table 2). MCM-41 exhibits a Type III isotherm (Fig. 2(c)) that is generally associated with weak absorption between the adsorbate (MCM-41) and the substrate (e.g. UFO). The weak absorption indicates that the substrate could not easily diffuse into the MCM-41 surface, thus suggesting that the MCM-41 could be formed by a non-porous structure. This also results in the low BET surface area detected for MCM-41. The low BET surface area shown by both PC and MCM-41 suggest that they could provide less reaction sites for pyrolysis cracking of UFO to occur and lead to low conversion of UFO into pyrolysis products.

3.1.2 Elemental composition

The AC and PC comprised mainly of carbon (67-71 wt.%; Table 2), which indicates that they are carbonaceous materials that have been reported to have a high value of dielectric loss tangent – an indication of high capability in absorbing and converting electromagnetic energy into heat (Fernandez et al., 2011; Menéndez et al., 2010). The dielectric loss tangent is an essential property that influences the heating rate and the maximum temperature that can be achieved by the material during microwave heating. The high values of dielectric loss tangent shown by AC (0.22-2.95) and PC (0.11-0.29) allow these materials to be rapidly heated to high temperature by microwave radiation through which microwave energy could penetrate the carbon and generates heat throughout the volume of the carbon (Dawson et al., 2008; Wu et al., 2008). Then, the heat generated can be used to heat neighboring substances to achieve a desired high temperature at a fast heating rate. This suggests that AC and PC can be used as an effective microwave absorbent to heat targeted material to achieve high temperature in order for pyrolysis cracking to occur.

The low carbon content of MCM-41 (5 wt.%; Table 2) suggests that it has a low value of dielectric loss tangent. This result is supported by a previous study which reported that silica-based material possessed a low value of dielectric loss tangent (≤ 0.05) and was considered as transparent to microwave radiation (Omar and Robinson, 2014). Nevertheless, the acidic properties and thermal stability of MCM-41 has been reported to aid in the cracking of hydrocarbons materials to produce liquid hydrocarbon fuels during pyrolysis process (Twaiq et al., 2003).

3.1.3 Pore size distribution

The pore size distribution of the microwave absorbent was examined to give information on the porosity of the materials. The porosity is the space that provides passage within a material to absorb molecules of equal or smaller in size. According to the IUPAC classification of pore size, macropores have a diameter of more than 50 nm, and the diameter of mesopores ranges from 2 to 50 nm, whereas micropores have a diameter of less than 2 nm. Absorption of small molecules normally occurs in micropores, while macropores and mesopores provide passage for absorbate to reach the micropores. In addition, the macropores and mesopores could act as transport arteries, making the internal parts of the material readily accessible to the molecules absorbed (Ryu et al., 1999; Zhao et al., 2015).

The average pore diameter of AC is 1.5 nm (Table 2), which is in the micropores range (< 2 nm). The AC shows a high proportion of micropore volume ($\sim 77\%$ of the total pore volume), indicating a high volume of wide micropores. The PC and MCM-41 showed mainly mesoporous structure with an average pore diameter of 2.2 nm and 12.4 nm respectively (Table 2). The results show that AC has a microporous structure that could provide many absorption sites to UFO in order for cracking reactions to occur during the pyrolysis. Combined with its

high BET surface area and potentially high value of dielectric loss tangent, this indicates that AC shows great potential as a microwave absorbent for use as the reaction bed material in microwave pyrolysis of UFO. Nevertheless, the use of materials with larger pore diameter (i.e. PC and MCM-41) as a reaction bed has been reported to improve the production of fuel products in the catalytic cracking of triglycerides-based materials such as palm oil (Twaiq et al., 2003). Thus, it was thought useful to investigate the effects of the use of materials of different characteristics (e.g. AC being microporous and PC and MCM-41 being mesoporous) on its performance as reaction bed to pyrolyze UFO by microwave heating.

3.2 Microwave pyrolysis of UFO

3.2.1 Temperature profile and heating performance during microwave pyrolysis using different microwave absorbent as the reaction bed

Microwave pyrolysis of UFO was performed over a range of process temperature (350 – 550 °C) using different microwave absorbents as both the heating medium and reaction bed. The resulting temperature profiles are shown in Fig. 3 to evaluate the heating rate generated from the use of the different bed of microwave absorbent.

The use of AC and PC showed a fast heating process (16 – 26 °C/min) to heat the UFO to achieve the targeted temperature for pyrolysis cracking. The process time taken for the heating and pyrolysis cracking of the UFO was fully completed in approximately 20 – 35 min. There was not much difference between the performance shown by the bed of AC and PC except with a slightly higher heating rate demonstrated by the PC bed. The fast heating rate corroborates the beneficial role of AC and PC being a carbonaceous material that can be rapidly heated to high temperature to pyrolyze UFO by microwave radiation (See Section 3.1.2). The represents a

desirable feature since the high heating rate could result in a high yield of bio-oil and low yields of solid residue and gaseous product (Gómez et al., 2016; Silva et al., 2016).

In contrast, MCM-41 bed showed a much slower heating process in which a lower heating rate (6-7 °C/min) and longer process time (45 to 100 min) was required for the microwave pyrolysis of UFO. Additionally, although the reaction was considered as completed as indicated from the time when the final drop of the condensed oil product was observed, there were still a sticky mixture of unpyrolyzed oil and MCM-41 remaining in the pyrolysis reactor. This indicates that MCM-41 bed has a lower ability to absorb the microwave energy required for the heating and pyrolysis cracking of UFO. This could be attributed to the low carbon content of MCM-41 (5 wt.%; Table 2) and the low dielectric loss tangent shown by mesoporous aluminosilicate materials (≤ 0.05).

3.2.2 Product yield

Pyrolysis products consisting of biofuel, pyrolysis gases and char residue were obtained, and the yield of these products over the range of process temperatures considered is presented in Fig. 4. Data are not recorded for temperatures of 300 °C and below, as although some pyrolysis conversion occurred and small amounts of pyrolysis volatiles were produced, no biofuel was observed after 1 h of reaction time; so the experiments were terminated.

At 350 °C, the solid mass remained in the reactor showed the highest yield (77-96 wt.%), yet it was found to be a mixture of unpyrolysed UFO and char residue. This could be attributed to the incomplete pyrolysis occurred at this temperature where some UFO were not thermally cracked to produce pyrolysis products. A higher temperature than 350 °C is thus required in order for a more extensive pyrolysis cracking to occur. At 400 °C above, the pyrolysis products

were dominated by biofuel (up to 73 wt.%) and smaller amounts pyrolysis gas (up to 35 wt.%). The reduction in the yield of biofuel at 500 °C and above can be explained by the secondary cracking and carbonization of the UFO (or the evolved pyrolysis-volatiles) to produce higher amounts of non-condensable pyrolysis gases and char residues, which can be observed from increased yield of both the pyrolysis gases and char residue. At 500 °C and above, the yield of pyrolysis gases was found to increase with the increase of temperature.

It was observed that use of AC and PC as the reaction bed showed a nearly similar product distribution. In contrast, the use of MCM-41 bed produced relatively lower amount of biofuel and pyrolysis gases. This could be attributed to the lower surface area of MCM-41 that provided less reaction sites for pyrolysis cracking of UFO. No pyrolysis volatile was observed even when the reaction time was extended up to 120 min. As a result, there were nearly ≥ 40 wt. % of UFO that remained unpyrolyzed and present in the form of a waxy mixture with the char residue in the reactor.

3.3 Biofuel

The biofuels obtained from the use of different beds of microwave absorbent under different pyrolysis temperatures were analyzed for their chemical composition, and the results are compared to the chemical composition of biodiesel and diesel; these are presented in Table 3. Data are not presented for the biofuel obtained at 350 °C and below, as although some pyrolysis conversion occurred and a small amount of biofuel was generated, it was decided to not collect the biofuel for analysis due to concern over the usefulness of the data obtained at these process temperatures where either incomplete or no pyrolysis conversion had occurred, and also the limitation involved in which the amount of the biofuel collected was insufficient to be analyzed by the various chemical analyses.

3.3.1 Elemental composition and calorific value

Carbon (71-81 wt.%) and hydrogen (11-14 wt.%) represented the main elements present in the biofuel, whereas oxygen (≤ 15 wt.%) and nitrogen (≤ 9 wt.%) were detected in low concentrations, and sulphur was not detected in the biofuel (Table 3). The amount of oxygen in the biofuel obtained using AC bed was lower compared to that obtained by the PC bed and zeolite bed, but in contrast it showed the highest carbon and hydrogen content (Table 3). The results coincide with the chemical compositions analyzed by GC-MS where the biofuel produced using AC showed the highest content of aliphatic hydrocarbon (up to 89 %) compared to that produced by PC bed (up to 88 %) and zeolite bed (up to 82 %) (Table 3). The nitrogen content was likely to derive from the food enhancer that was used and transferred to the cooking oil during the frying process. The production of biofuel with a low nitrogen content and that is free of sulphur represents a favourable feature in producing a potential fuel source with low or zero emissions of NO_x and SO_x during the use of the fuel in combustion process.

Calorific value indicates the energy content of a material. The calorific value of the biofuel obtained (40-46 MJ/kg) is close to the calorific value reported for petroleum-based fuel (42-46 MJ/kg) (Sanjid et al., 2013), indicating that biofuels with high combustion energy can be obtained by the pyrolysis performed using a reaction bed approach.

3.3.2 Hydrocarbon composition

The biofuel produced using AC bed comprised of C₁₀-C₂₀ aliphatic hydrocarbons (76-89 %), small amounts of ketones (1-6 %) and aldehydes (4-6 %). At a pyrolysis temperature of 400 °C, heavier hydrocarbon components (C₁₆-C₂₀ hydrocarbons) showed higher concentration (66 %), but the productions of lighter hydrocarbon components (C₅-C₁₅ hydrocarbons) (54-72 %)

were increased as the pyrolysis temperature was performed at 450 °C and above. This can be attributed to the cracking of heavier hydrocarbons components into lighter hydrocarbons components at higher temperatures. Interestingly, no carboxylic acid and low amounts of oxygenated compounds such as aldehydes (≤ 6 %) and ketones (≤ 4 %) was detected in the biofuel obtained by AC bed. This could be attributed to the decarbonylation of oxygenated compounds originally present in the UFO (e.g. carboxylic acids, Table 1) into aliphatic hydrocarbons (Boey et al., 2011; Hancsók et al., 2012; Mikulec et al., 2010).

It was likely that the triglycerides and fatty acids originally present the UFO (Table 1) have undergone pyrolysis cracking via a free-radical mechanism to produce hydrocarbon radicals as has been reported by Lam et al. (2016) in microwave pyrolysis of waste oil (Lam et al., 2016a). This mechanism is likely to have led to the production of hydrocarbon radicals that were stabilised by capturing the hydrogen atoms from nearby or same molecules, producing alkanes and alkenes via H-atom abstraction and β -scission reactions. Heavy alkanes and alkenes were then cracked to form lighter compounds. This resulted in the conversion of larger hydrocarbons in the UFO to produce smaller hydrocarbon chains.

The bio-oil obtained using PC bed consisted of mainly C_{11} - C_{20} hydrocarbons (73-88 %) and small amounts of carboxylic acids (5-10 %). In particular, the carboxylic acid content was reduced with the increase of pyrolysis temperature, indicating that higher temperatures could have promoted reactions such as decarbonylation to convert carboxylic acids into aliphatic hydrocarbons. The use of MCM-41 bed produced a bio-oil comprising mainly of C_{11} - C_{20} aliphatic hydrocarbons (40-51 %) and smaller amounts of aromatic (7-15 %) and carboxylic acids (6-11 %). The aromatics (e.g. benzenes) were likely to be formed via Diels-Alder type

secondary reactions, which involve dehydrogenation and cyclisation of alkenes (produced from pyrolysis cracking of UFO) to form aromatics (Lam et al., 2012a; Omar and Robinson, 2014).

It was revealed that AC bed produced the most desirable biofuel over the types of microwave absorbents considered, showing a desirable composition dominated by light C₅-C₁₅ hydrocarbons with no carboxylic acid and low amounts of oxygenated compounds, thus representing a suitable microwave absorbent to be used to form the reaction bed for pyrolysis treatment and recovery of UFO. The light C₅-C₁₅ hydrocarbons represents a potential fuel source since they are within the hydrocarbon range for petrol and diesel fuel (Capunitan and Capareda, 2012), and the absence of carboxylic acids with low amounts of oxygenated compounds could reduce the formation of oxygenated by-products that could generate undesirable acidic tar or sludge in the biofuel. The amount of oxygenated compounds (e.g. carboxylic acids, ketones, aldehydes) in the biofuel (≤ 11 %) were significantly lower compared to those obtained by conventional pyrolysis of vegetable oil (44-71 %) (Lappi and Alén, 2009; Phung et al., 2015).

3.4 Energy recovery

Fig. 5 presents the energy recovered in the pyrolysis products (biofuel, pyrolysis gases and char) from UFO. The energy recovery was estimated based on the calorific value of UFO and pyrolysis products using the following formula:

$$\text{Energy Recovery} = \frac{[(\text{Product weight} \times \text{Product's calorific value}) \times 100]}{(\text{Weight of UFO} \times \text{UFO's calorific value})} \quad [1]$$

Calorific value of pyrolysis gases was estimated based on Total Ion Content percentage (TIC%) of gaseous hydrocarbons (e.g. CO, H₂, CH₄, and light hydrocarbons) detected in the

pyrolysis gases obtained from previous study (Chen et al., 2014b). The estimation of calorific value is based on the following formula:

$$\text{Calorific value of pyrolysis gases} = \text{TIC\%} \times \text{gross calorific value of compounds obtained from NIST Chemistry Web Book} \times \text{gas yield}/100. \quad [2]$$

The biofuel showed a calorific value of 40 to 46 MJ/kg, whereas the calorific value determined for char ranged from 12 to 32 MJ/kg over the range of process temperatures considered. The data obtained at a process temperature of 450 °C and above were presented in this analysis where a higher yield of biofuel was obtained at these temperatures compared to that obtained at other process temperatures (see Fig. 4, Section 3.2.2).

The use of AC bed showed the highest energy recovery (88-90%) followed by the use of PC bed (76-83 %) and MCM-41 bed (54-59 %). The energy recovered by the biofuel obtained from microwave pyrolysis using a reaction bed of microwave absorbent in this study (~37-83%) is significantly higher than that obtained by the biofuel from a previous study on microwave pyrolysis of rapeseed oil performed with no microwave absorber (~17%) (Omar and Robinson, 2014). Energy loss was observed in this pyrolysis operation and could be attributed to the heat loss from the reactor and the condensation system that occurred during the pyrolysis process. Pyrolysis at 500 °C using AC and PC as the reaction bed showed the highest energy recovery of pyrolysis products ($\geq 83\%$), whereas the use of MCM-41 bed showed the highest energy recovery at 550 °C (59%).

3.5 Scale-up potential for industrial application

In view of the mainly positive results obtained in this study, it would be worthwhile to scale up the laboratory-scale operation in order to test the reliability and practicality of this pyrolysis approach for industrial applications that deal with large amounts of waste material. This section expands some of the developmental work that can be performed to scale up the pyrolysis approach, and it is hoped that the work would serve as the groundwork for the development of a commercially-viable process.

It is proposed that most of the components in the scaled-up prototype should remain the same as those used in the configuration of the lab-scale microwave pyrolysis apparatus in terms of their functions rather than their sizes. However, some modifications to the design and configuration of the existing apparatus are needed in order to avoid or reduce unnecessary costs in the process operation. The existing apparatus uses a conventional microwave oven as the heating source for the pyrolysis operation. It would not be feasible to contemplate heating a much larger reactor by placing it within a scaled-up microwave oven. Thus, it is envisaged that future work could be performed by replacing the conventional microwave oven with a magnetron system comprising of conventional microwave heating components, consisting of a power supply and a magnetron to generate microwave radiation, and waveguides to channel the direction of microwaves, but excluding the microwave applicator (the metal chamber where microwaves meet and heat the material to be processed). The microwave radiation generated from the magnetron system could then be channeled into the reactor through the use of commercial waveguides. The approach of excluding the microwave applicator from the process configuration provides a more energy-efficient heating process as the microwave energy is

targeted only to the reactor and not to other empty spots within the applicator or the applicator itself.

With respect to the size of the scaled-up reactor, it is proposed that the reactor should be designed based on some of the useful data obtained from the results presented in this study. The existing lab-scale apparatus, which contains a reactor with a volume of ~1.5 litres, is capable of processing a maximum of approximately 1 kg/batch of waste oil. Therefore, in order to scale up the process to a level suitable for pilot plant operation, which might typically operate at a processing capacity of 1 ton/batch, a reactor with a volume of 1500 litres might be required. Thus, it is proposed that a cylindrical vessel with a height of 1 m and a diameter of 0.7 m is suitable to produce a reactor with a volume of about 1540 litres.

The other main components in the scaled-up prototype can remain mostly the same as those used in the configuration of the existing microwave pyrolysis apparatus. It is proposed that thermocouple should continue to be used for temperature measurement due to their simplicity and low cost, although there are complex systems that can give a more accurate measurement of temperature in microwave systems. The reliable temperature readings shown by the thermocouple in this study make it a good alternative compared to other more expensive and complicated methods. It is evident from the results presented in this study that the existing condensation and collection system provided a very efficient way and showed a good performance in recovering the biofuel products generated from the pyrolysis experiments; the system is capable of condensing up to 73% by weight of the UFO into oil product. Thus, it is envisaged that a similar design could be used in the scaled-up prototype for the recovery of biofuel products. Efforts should also be made to increase the amount of energy that can be recovered from the system. This can be achieved through the use of microwave-transparent heat

insulating fibre material to fully insulate the reactor and associated fittings in order to recover energy loss from the prototype reactor, and the use of heat integration systems to recover energy during the cooling of the products in the condensation system.

Following the construction of the scaled-up prototype, it is envisaged that future work could be performed to explore the other process parameters (e.g. heating rate, amount of microwave power output) that may have an influence on the outcome of the pyrolysis operation in order to assess the feasibility of the pyrolysis process for large scale application. In addition, a study could be performed to investigate the feasibility of pyrolysing UFO in a continuous operation (i.e. continuous addition of waste oil to the reactor at a given flow rate). Continuous operation is preferred in improving the industrial feasibility of this pyrolysis approach. In a continuous process, there is a continuous and steady flow of reactants (e.g. waste oil) into the reactor, and a continuous recovery of products out of the reactor from the conversion of the reactants. A continuous operation can offer a number of advantages over batch operation, e.g. simplified automatic control, reduced labour costs, and since there are constant operating conditions, thus the possibility of providing better control of quality. Furthermore, work should be performed to investigate different operational protocols with a view to enhancing the recovery of desired pyrolysis products and to maximise the concentrations of valuable compounds in the products, particularly the biofuel product due to its great potential for use as a liquid fuel.

4. Conclusion

Activated carbon showed a microporous structure and was detected to have a high surface area and high carbon content (an indication of high capability in absorbing and converting microwave radiation into heat). These results suggest that AC can be used as an effective microwave absorbent to heat targeted material to achieve high temperature for pyrolysis

cracking while simultaneously providing many reaction sites for cracking reactions to occur, resulting in potentially high conversion of targeted material into pyrolysis products.

This study reveals that the use of both activated carbon and particulate carbon as a reaction bed showed a fast heating process (16 – 26 °C/min) to heat the UFO to achieve the targeted temperature for pyrolysis cracking, representing favorable features that could lead to short process time and less energy usage. The use of activated carbon bed produced the highest yield of biofuel (73 wt%) over the types of microwave absorbents considered, showing a desirable composition dominated by light C₅-C₁₅ hydrocarbons with low contents of oxygenated compounds and nitrogen. The oil product showed a high calorific value (46 MJ/kg) that is nearly comparable to petroleum-based fuel and was also free of carboxylic acid and sulphur, thus representing a potential source of bioenergy to be upgraded for use as a ‘cleaner’ biofuel with potentially reduced oxygenated by-products plus low or zero emissions of NO_x and SO_x during the use of the fuel in combustion process.

The use of activated carbon bed also showed the highest energy recovery (88-90%) from used frying oil compared to that shown by the use of particulate carbon (76-83 %) and MCM-41 (54-59 %) as the reaction bed. Our results demonstrated that activated carbon represents a suitable microwave absorbent to be used to form the reaction bed for microwave pyrolysis of used frying oil, and the use of a microwave-heated reaction bed of activated carbon shows exceptional promise as an improved pyrolysis approach to convert UFO to produce a biofuel produce with desirable properties. By recycling the UFO, this maximizes the use of existing resources while preventing the release of such waste materials to the environment. This pyrolysis approach and its unique combination of properties (e.g. fast heating rate, extensive cracking capacity, high yield of desirable biofuel) enables the generation of significant value out of what

would otherwise be a troublesome waste for disposal, thus contributing to redesigning human behavior for sustainability.

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Table 2 Characteristics of microwave absorbents used as reaction bed material

Table 3 Chemical composition of biofuels

Table 1

Compositions and characteristics of UFO

Oil properties	UFO derived from palm oil
Elemental composition (wt.%)	
C	71.2
H	13.3
N	0.8
S	0
O ^a	14.7
Calorific value (MJ/kg)	39.2
Chemical composition(%)	
Aliphatic hydrocarbons (C₁₀-C₁₆)	58
Carboxylic acids (C₁₆H₃₆O₂ -C₁₈H₃₂O₂)	30
Other unidentified compounds	12

Table 2

Characteristics of microwave absorbents used as reaction bed material

	PC	AC	MCM-41
Elemental analysis (wt.%)			
C	71	67	5
H	0.1	4	0.4
N	0.3	3	0.2
S ^a	0	0	0
O ^b	29	26	94
Particle size (mm)	0.5 - 5.0	0.5 - 3.0	0.3 - 2.0
BET surface area, S_{BET} (m²/g)	7.18	850	6.13
Total pore volume, V (cm³/g)	0.004	0.318	0.019
Micropore volume (cm³/g)	0.001	0.244	0.0006
Average pore diameter ^c (nm)	2.2	1.5	12.4

^a Sulphur content is not detectable by the minimum detection limit of the CHNS analyser (<0.05 wt%), and thus it is assumed to be 0 wt% in calculation.

^b Calculated by difference.

^c Also known as absorption pore width, calculated by $4 V/S_{BET}$ (Chen et al., 2014).

Table 3

Chemical composition of biofuel.

Biofuel properties	Biofuel at different process temperatures												Biodiesel ^a	Diesel ^b
	AC bed				PC bed				MCM-41 bed					
	400°C	450°C	500°C	550°C	400°C	450°C	500°C	550°C	400°C	450°C	500°C	550°C		
Elemental analysis (wt.%)														
C	75.7	80.1	79.4	80.5	77.2	79.0	76.9	73.5	72	72	73	71	77	87
H	13.3	13.5	13.6	14.4	14.0	14.1	13.9	11.1	12	12	13	13	12	13
N	1.4	1.1	1.1	1.1	1.7	1.7	2.1	1.0	9.0	3.0	1.5	0.8	-	-
S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	-	-
O	9.6	5.3	5.9	4.0	7.1	5.2	7.1	14.3	7.0	13	12.5	15.2	11	0
Calorific value (MJ/kg)	41	46	46	46	43	43	41	40	40	41	41	40	37-43	45
Chemical compositions (peak area %)														
Aliphatic hydrocarbons	76	79	89	88	73	80	87	88	75	82	81	81	-	-
Aromatics	-	-	-	-	-	-	-	-	15	11	7	10	-	-
Carboxylic acids	5	-	-	-	10	8	6	5	11	6	6	7	-	-
Ketones	6	1	-	5	-	-	1	-	-	-	-	-	-	-
Aldehydes	-	4	4	6	-	-	-	-	-	-	-	-	-	-
Carbon components (peak area %)														
C ₅ -C ₁₀	-	8	18	9	-	-	-	-	-	-	-	-	-	-
C ₁₁ -C ₁₅	10	46	44	63	45	50	55	61	47	51	40	40	1	100
C ₁₆ -C ₂₀	66	27	27	16	28	30	32	27	43	42	48	51	98	-

^aASTM D6751 specifications of biodiesel (Atabani et al., 2013; Farooq et al., 2013; Ong et al., 2011)^bASTM D975 specifications of diesel (Capunitan and Capareda, 2012; Ong et al., 2013)

(-) not available

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Fig. 1 Schematic drawing of the microwave pyrolysis apparatus. (1) Nitrogen gas, (2) Flowmeter, (3) Electronic temperature controller, (4) Microwave oven, (5) Quartz reactor, (6) Stirrer, (7) 1st collecting vessel, (8) Vigreux column, (9) Liebig condenser, (10) 2nd collecting vessel, (11) Ice bath.

Fig. 2 Adsorption and desorption isotherms of (a) AC, (b) PC, and (c) MCM-41.

Fig. 3 Temperature profile during microwave pyrolysis of UFO using (a) AC bed, (b) PC bed, and (c) MCM-41 bed. Pyrolysis was performed in the presence of 150 g of microwave absorbent.

Fig. 4 Product yield from microwave pyrolysis of used frying oil performed at different process temperatures using (a) AC, (b) PC , and (c) MCM-41 as reaction bed

Fig. 5 Energy recovery of pyrolysis products from UFO

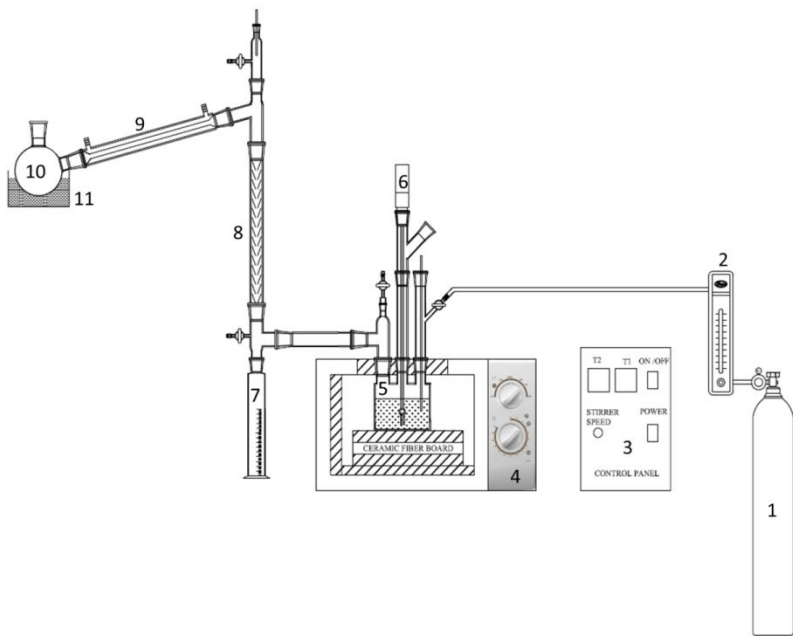


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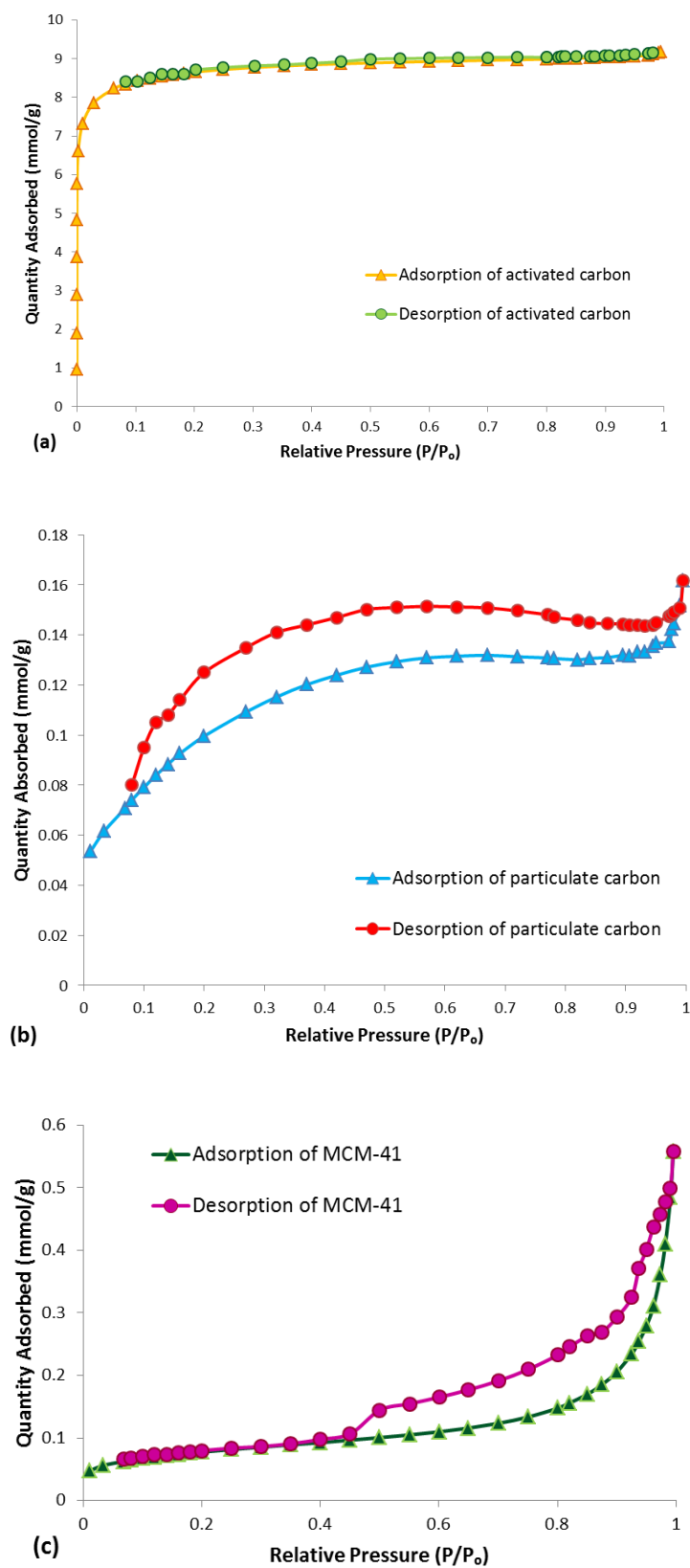


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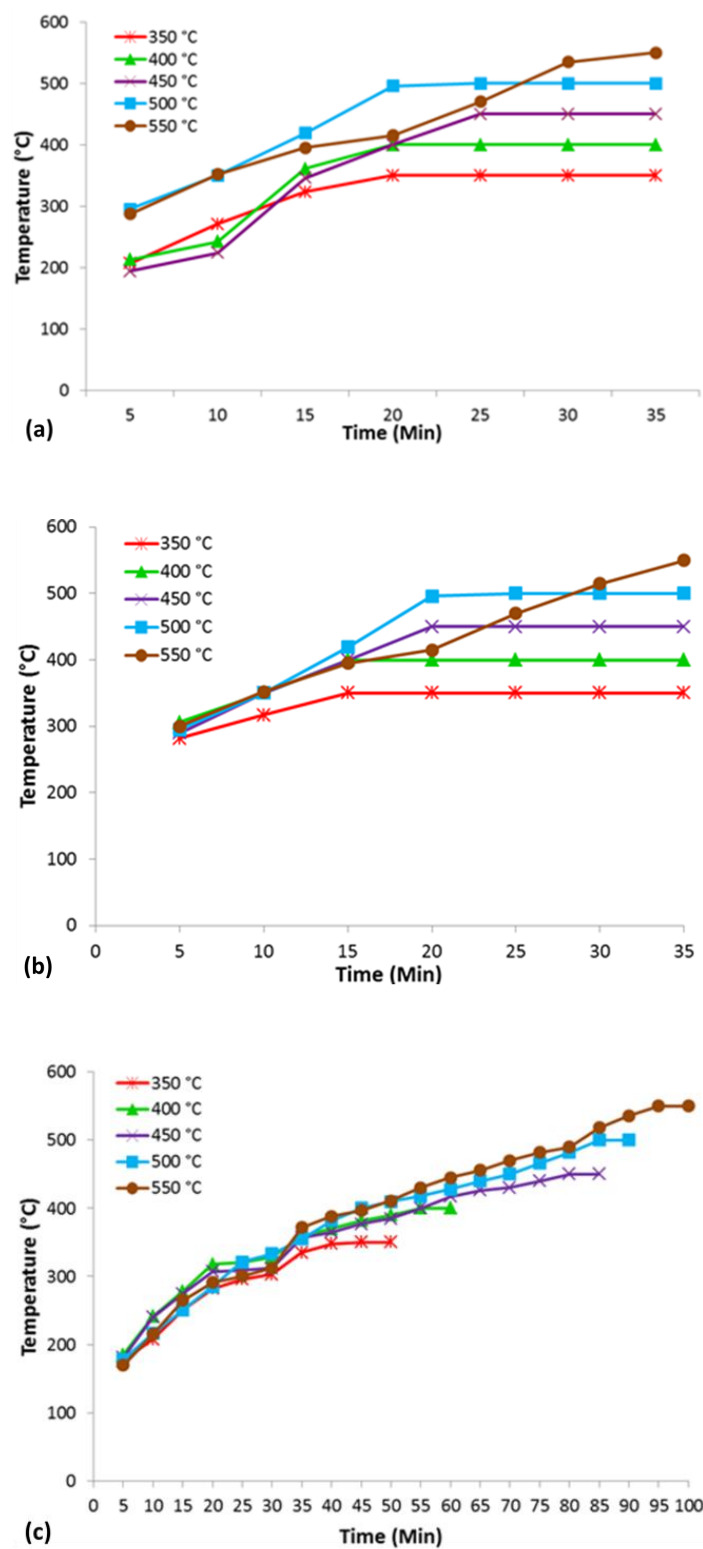


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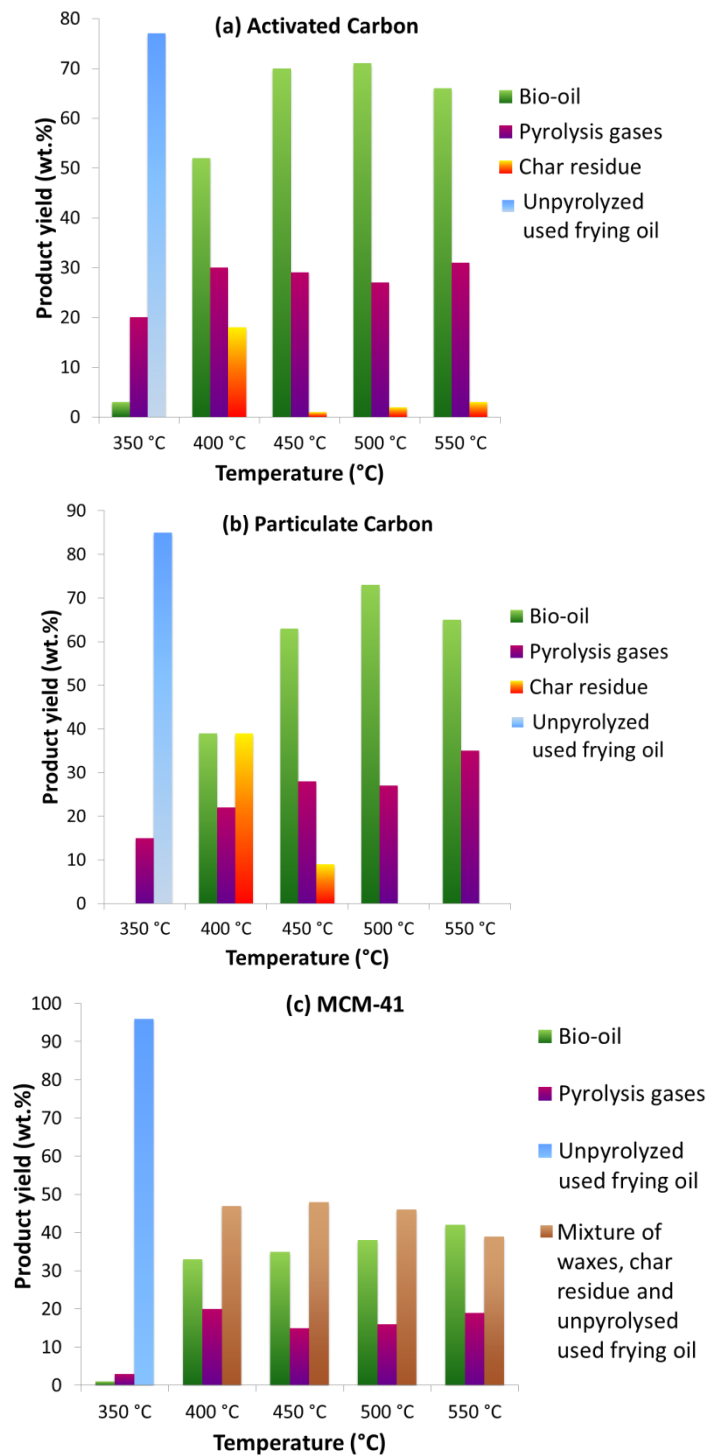


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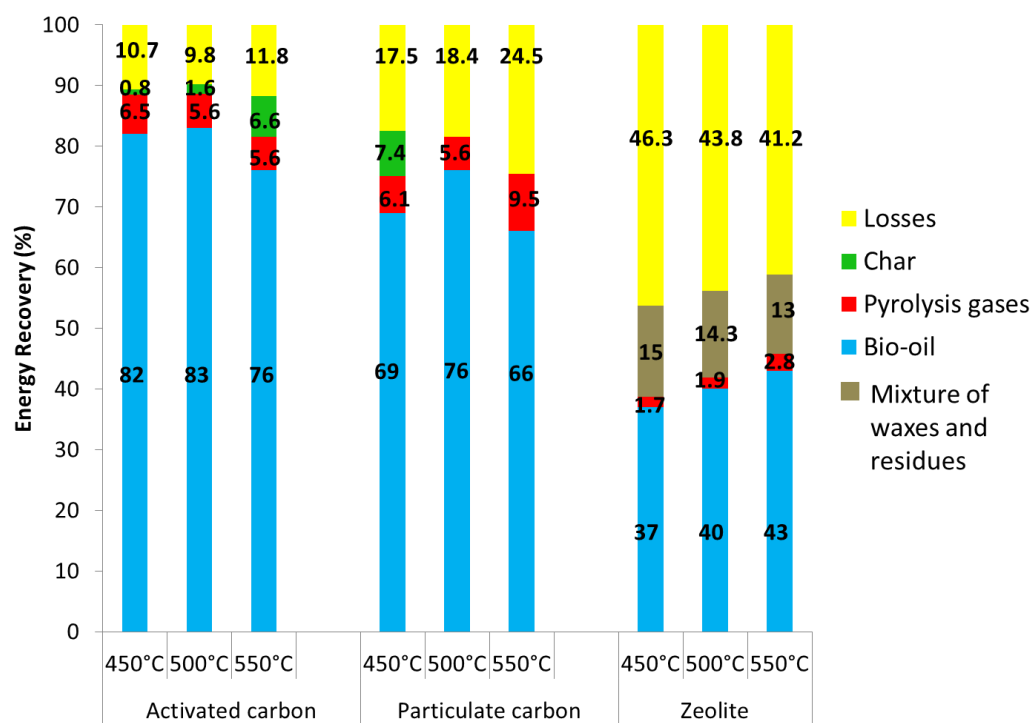


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